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Toyoda et al.

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(54) **THERMOELECTRIC CONVERSION
ELEMENT AND PRODUCING METHOD
THEREOF**

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CPC **H01L 35/04** (2013.01); **H01L 35/16**
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(2013.01)

(58) **Field of Classification Search**

CPC H01L 35/04; H01L 35/34; H01L 35/32

USPC 136/225

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,930,303 A 1/1976 Alais et al.

5,055,140 A 10/1991 Kumada et al.

(Continued)

FOREIGN PATENT DOCUMENTS

CN 101840989 A 9/2010

DE 10232376 A1 * 2/2004 H01L 35/32

(Continued)

OTHER PUBLICATIONS

DE 10232376 A1, Machine Translation, Feb. 2004.*

(Continued)

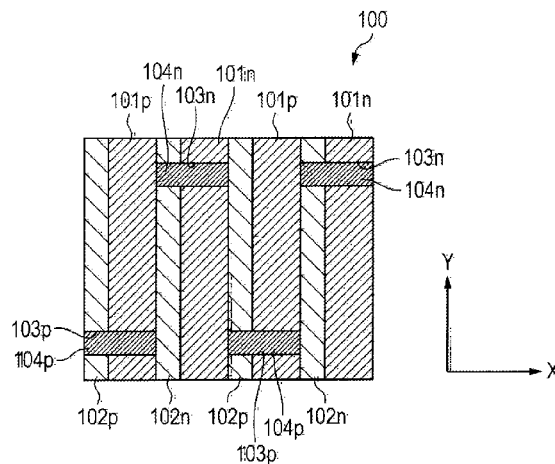
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(57) **ABSTRACT**

The invention provides a thermoelectric conversion element having a lot of pn junction pairs per unit area and having a thermoelectric material chip which is hardly broken, and a producing method thereof. In the thermoelectric conversion element of the invention, plural substrates in each of which a film-shaped thermoelectric material is formed in a surface thereof are disposed. As a result, because the number of pn junction pairs per unit area is increased, a high output can be obtained. Because the thermoelectric material is formed into the film shape, reliability degradation caused by a breakage of the thermoelectric material can be prevented, even in the thermoelectric material having many pn junction pairs per unit area, namely, a sectional area is small.

8 Claims, 9 Drawing Sheets



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- (56) **References Cited**

U.S. PATENT DOCUMENTS

6,043,423	A	3/2000	Satomura et al.
6,274,803	B1	8/2001	Yoshioka et al.
2005/0178424	A1	8/2005	Yotsuhashi et al.
2008/0163916	A1	7/2008	Tsuneoka et al.
2010/0116308	A1	5/2010	Hayashi et al.

FOREIGN PATENT DOCUMENTS

JP	50-141287	11/1975
JP	1-93182	4/1989
JP	8-222770	8/1996
JP	10-303471	11/1998
JP	11-274581	10/1999
JP	2001-119076	4/2001

JP	3592395	B	9/2004
JP	2006-86510		3/2006
JP	3927784	B	3/2007
JP	3958857	B	5/2007
JP	2008-205181		9/2008
JP	2009-246296		10/2009
JP	2011-199091		10/2011
WO	2005/047560		5/2005

OTHER PUBLICATIONS

English translation of Search Report dated on Mar. 27, 2015 for the related Chinese Patent Application No. CN2012800044600.

Partial English Translation of "Some Considerations on Thermoelectric Cooling Device", Yoshihiko Ogawa et al., IEICE Transactions C-2 vol. J75-C-2 No. 8 pp. 416-424, Aug. 1992.

Partial English Translation of "Development and research of thermoelectric module on Bi—Te based thin film", Kitagawa Industries Co Ltd. and AIST, pp. 24-25, Aug. 2003.

International Search Report of PCT Application No. PCT/JP2012/000376 dated Jun. 27, 2012.

* cited by examiner

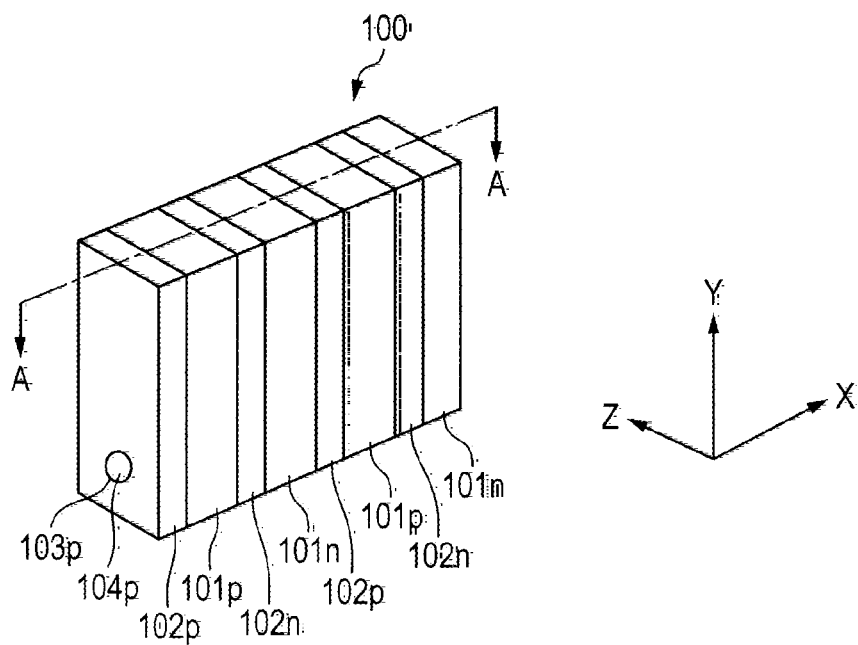


FIG. 1A

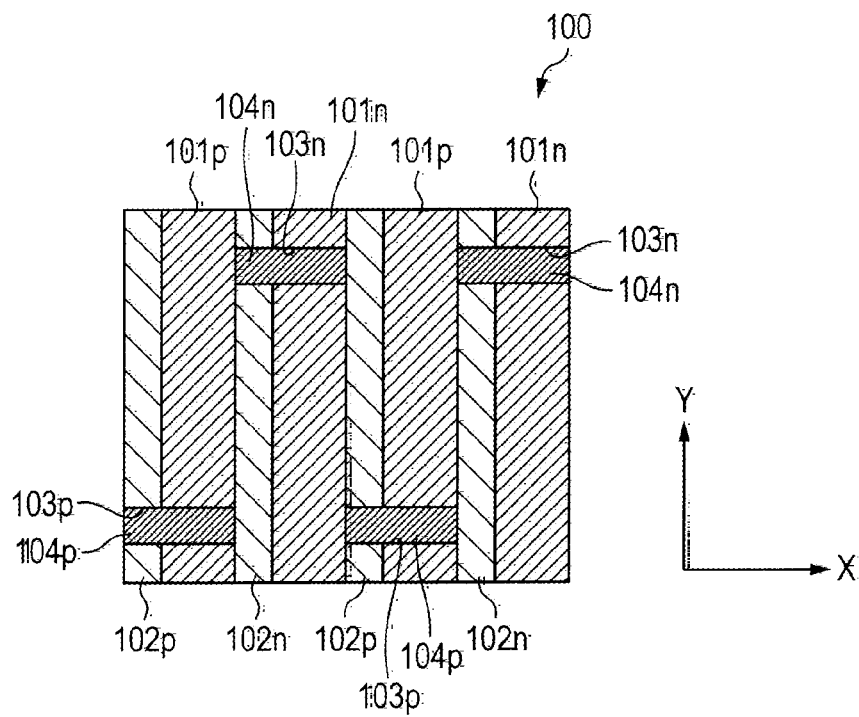


FIG. 1B

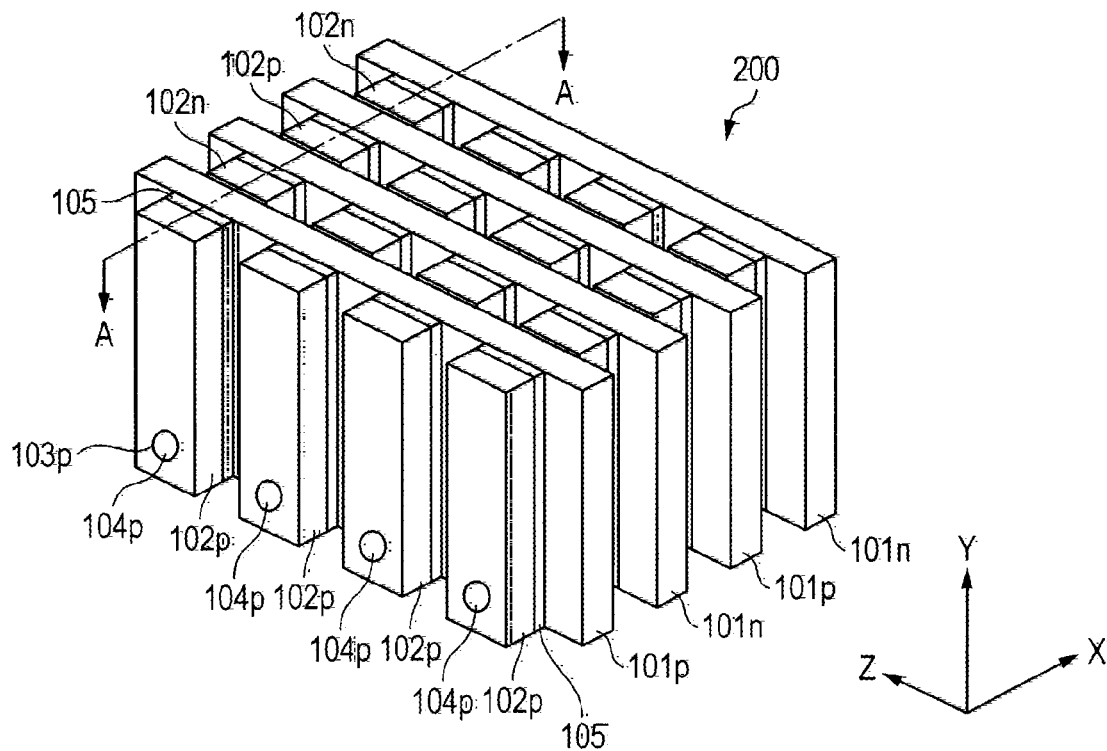


FIG. 2A

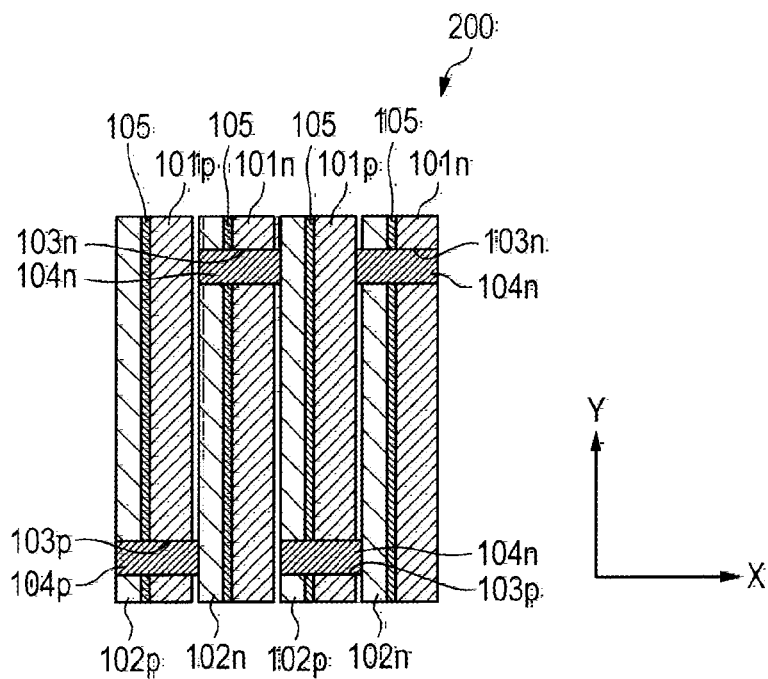


FIG. 2B

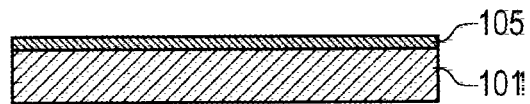


FIG. 3A

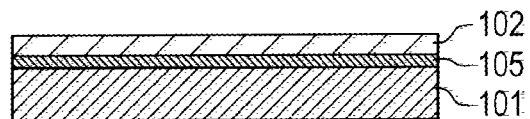


FIG. 3B

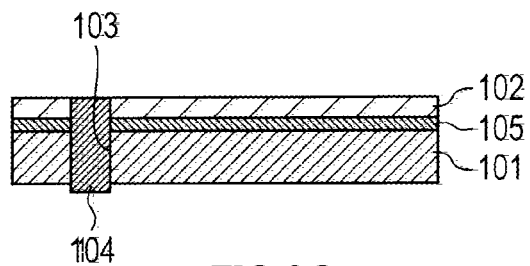


FIG. 3C

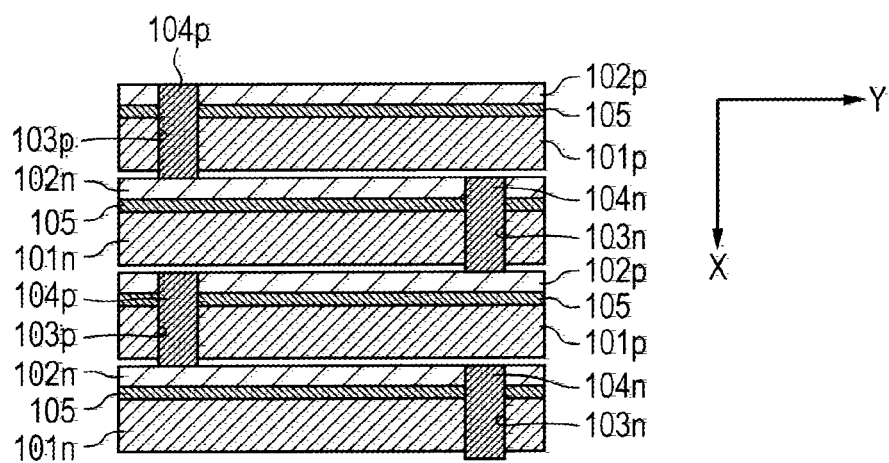


FIG. 3D

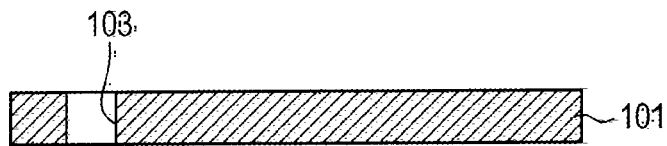


FIG. 4A

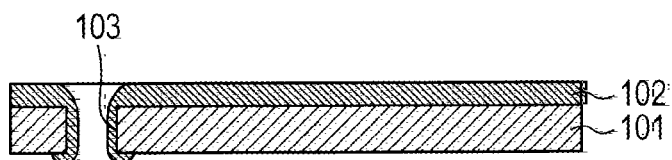


FIG. 4B

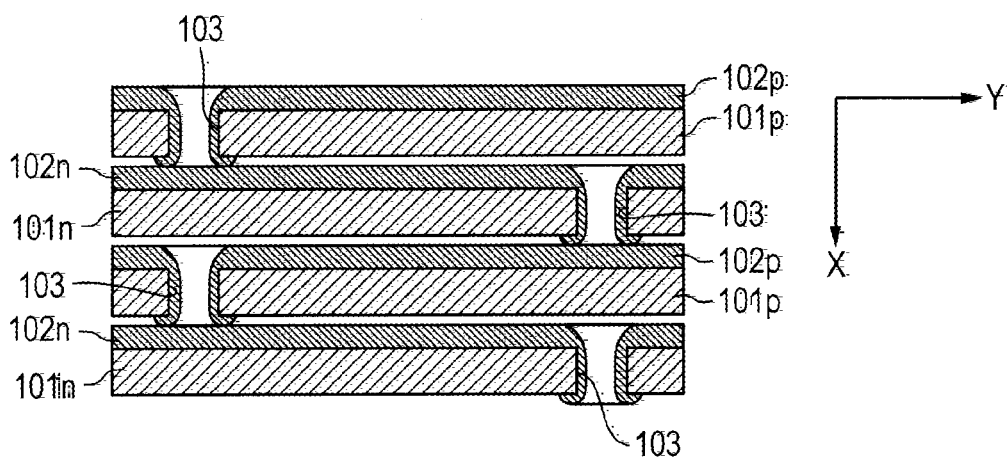


FIG. 4C

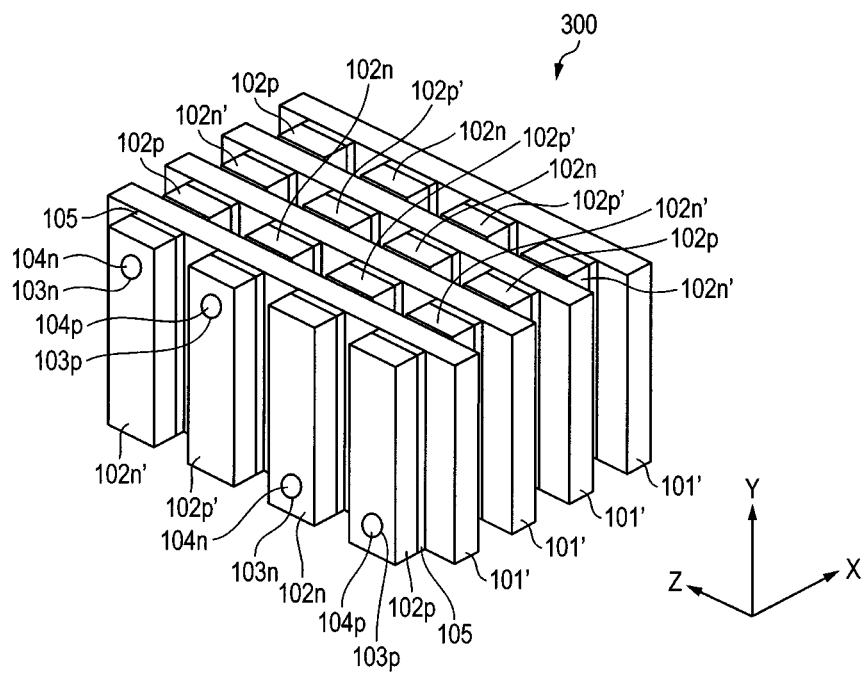


FIG.5

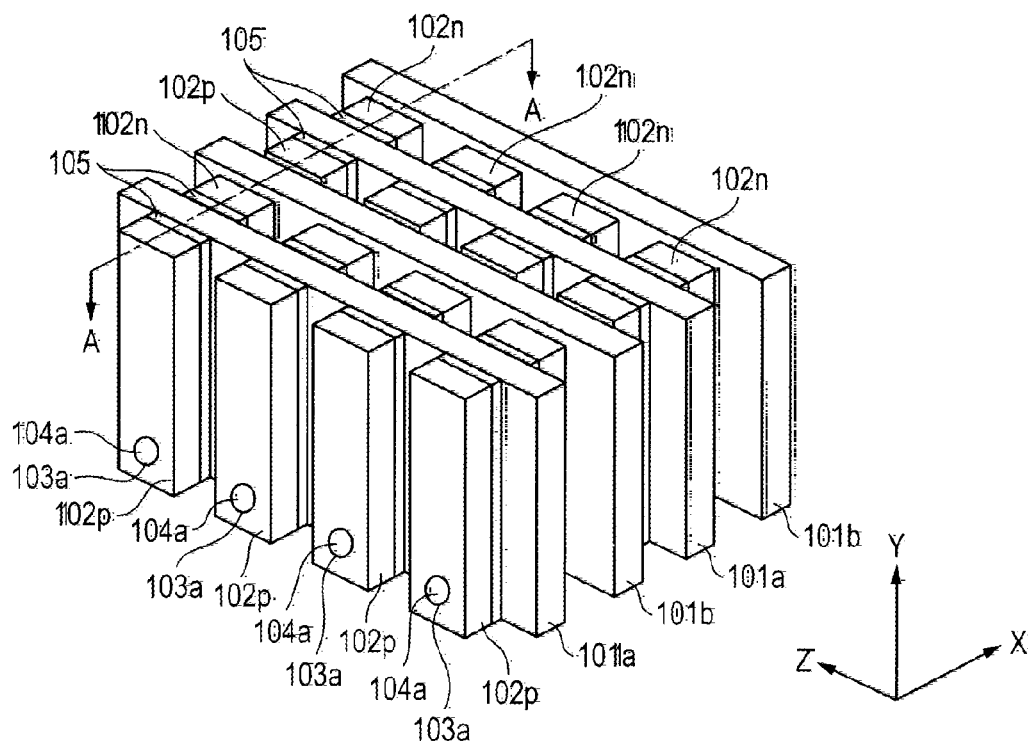


FIG.6A

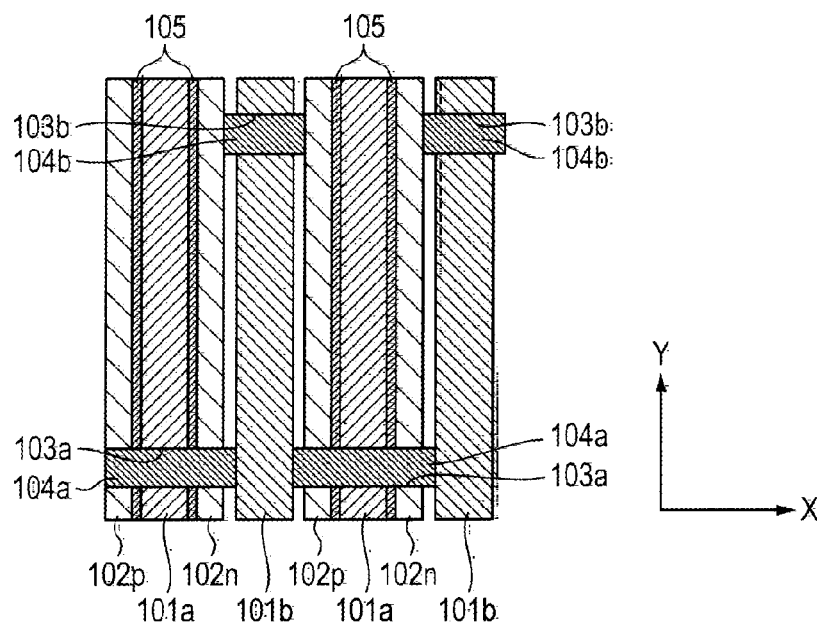


FIG.6B

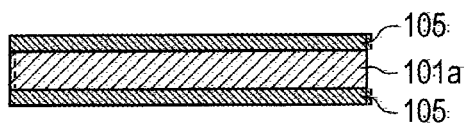


FIG. 7A

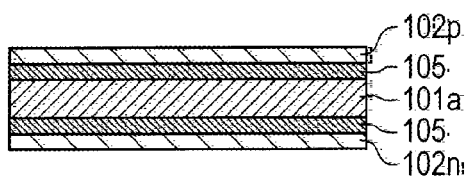


FIG. 7B

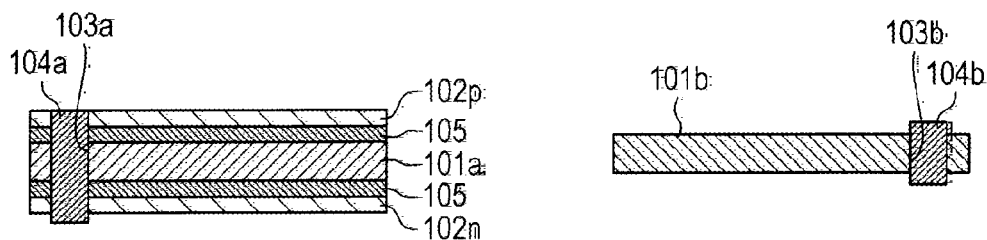


FIG. 7C

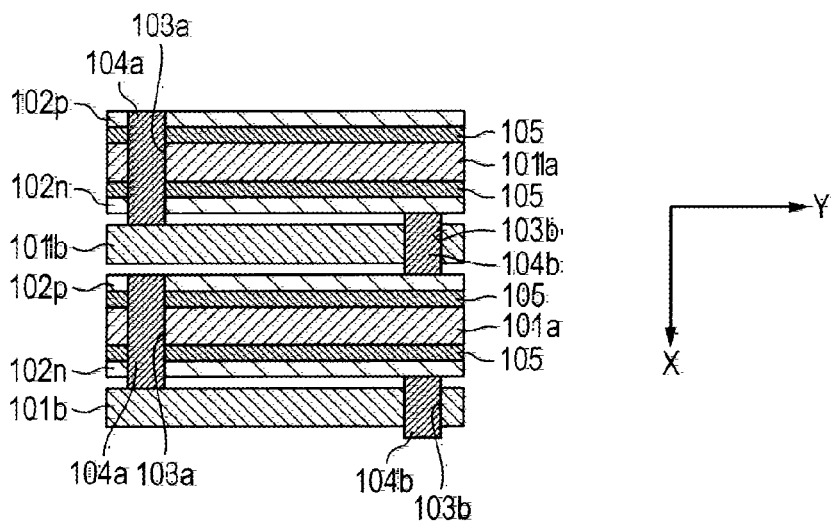


FIG. 7D

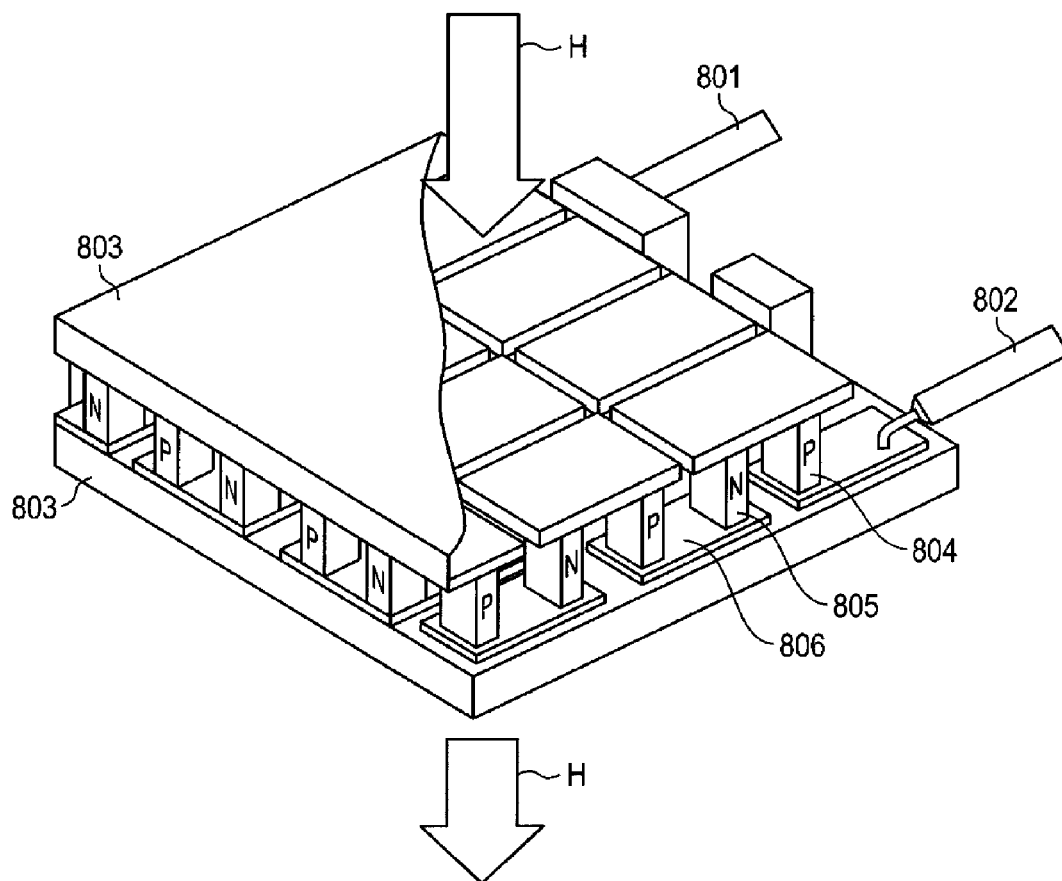


FIG. 8 PRIOR ART

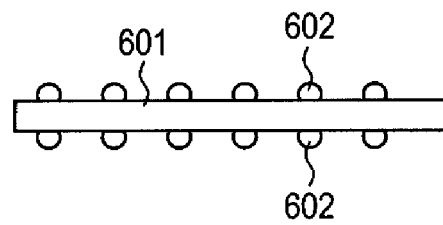


FIG. 9(a) PRIOR ART



FIG. 9(b) PRIOR ART

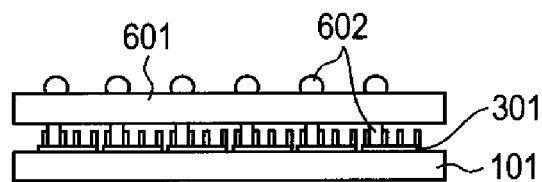


FIG. 9(c) PRIOR ART

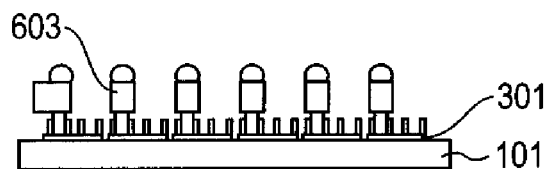


FIG. 9(d) PRIOR ART

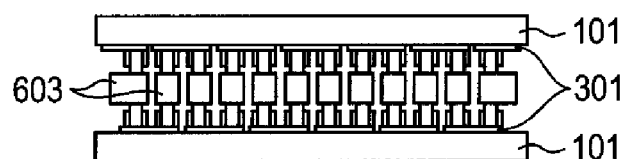


FIG. 9(e) PRIOR ART

1

THERMOELECTRIC CONVERSION ELEMENT AND PRODUCING METHOD THEREOF

TECHNICAL FIELD

The present invention relates to a thermoelectric conversion element and a producing method thereof.

BACKGROUND ART

An element in which a Peltier effect or a Seebeck effect is utilized is used as a thermoelectric conversion element. The thermoelectric conversion element has a simple structure, and the thermoelectric conversion element is easily handled to be able to maintain a stable characteristic. Therefore, the thermoelectric conversion element attracts attention of a wide variety of applications. Particularly, because the thermoelectric conversion element can perform to cool a limited part and to control a temperature of the limited part near room temperature, accurately, as an electronic cooling element, researches are widely conducted toward applications of optoelectronics and an isothermal treatment of a semiconductor laser.

Conventionally, as illustrated in FIG. 8, in configuration of the thermoelectric conversion element used in electronic cooling and thermic generation. Plural pn junction pairs are arrayed in series, the pn junction pair being configured so that p-type thermoelectric material **804** is in contact with n-type thermoelectric material **805** through junction electrode **806**. In FIG. 8, the sign **803** designates a substrate, the sign **801** designates a current introduction terminal (positive electrode), the sign **802** designates a current introduction terminal (negative electrode), and the sign H designates an arrow that indicates a heat flow direction. The thermoelectric conversion element illustrated in FIG. 8 is configured such that, depending on a direction of a current passed through a junction portion, one end portion is heated while the other end portion is cooled.

A material that has a large performance index Z in a usage temperature range is used as the thermoelectric conversion element. The performance index Z is expressed by a Seebeck coefficient " a " that is of a unique constant of a substance, a specific resistance " r ", and a thermal conductivity " K " ($Z=a^2/rK$). Usually, a Bi_2Te_3 system material is used in the thermoelectric conversion element, and a crystal of the Bi_2Te_3 based material has a significant cleavage property. Therefore, when the thermoelectric conversion element is subjected to processes such as slicing and dicing in order to obtain the thermoelectric conversion element from an ingot, a yield may be significantly degraded due to a crack and a chip.

The following method is attempted to solve the problem. The method is for producing a thermoelectric conversion module comprising the steps of: mixing, a material powder having a desired composition; heating and melting the material powder; solidifying the melted material powder to form a solid solution ingot of a thermoelectric semiconductor material having a rhombohedral structure (hexagonal structure); crushing the solid solution ingot to form solid solution powders; homogenizing particle diameters of the solid solution powders; pressurizing and sintering the solid solution powders whose particle diameters are homogenized; and, plastically deforming and flattening the powder sintered body under a hot condition to orient a crystal of the powder sintered body toward a crystal orientation in which an excellent performance index is obtained (a step of hot upset forging) (for example, see PTL 1).

2

A shape of each thermoelectric material chip used as the thermoelectric conversion element is a cuboid whose one side ranges from hundreds micrometers to several millimeters. Recently, in the thermoelectric conversion element that is used under near room temperature including a temperature difference of tens degrees, it is said that the thermoelectric conversion element having the size and thickness of tens to hundreds micrometers has high performance (for example, see NPL 1).

The number of pn junction pairs in one thermoelectric conversion element is up to hundreds, and density of the pn junction pair is up to tens pairs/cm². Increasing the number of pn junction pairs becomes a necessary factor in order to improve thermoelectric conversion performance and in order to extend applications of the thermoelectric conversion element. Particularly, in power generation in which a small temperature difference is utilized, a generated electromotive force is proportional to the number of pn junction pairs. Therefore, desirably the number of pn junction pairs that are connected in series in the thermoelectric conversion element is increased as many as possible in order to take out a high voltage from the thermoelectric conversion element.

In the case in which the thermoelectric conversion element is used as a cooling element or a temperature control element, a current passed through the thermoelectric conversion element is increased with decreasing number of series-connected thermoelectric material chips. Therefore, it is necessary to make wiring or a power supply larger. Accordingly, desirably the number of series-connected thermoelectric material chips is increased as many as possible.

FIGS. 9A to 9E illustrate a conventional method for producing the thermoelectric conversion element in which the number of thermoelectric material chips per unit area (chip density) is increased while the size of the thermoelectric material chip is reduced.

In a bump forming process (a), solder bumps **602** are formed in both surfaces of plate-like or rod-shaped p-type or n-type thermoelectric material wafer **601**. In an electrode wiring process (b), electrode wiring **301** is formed in a surface of substrate **101**. In connecting process (c), thermoelectric material wafer **601** in which solder bumps **602** are formed through the bump forming process (a) is disposed in the face of substrate **101**. Then electrode wiring **301** on substrate **101** and thermoelectric material wafer **601** are connected by soldering. FIG. 9C illustrates the connecting of p-type or n-type thermoelectric material wafer **601** and electrode wiring **301** on substrate **101**. For example, when FIG. 9C illustrates the connecting of p-type thermoelectric material wafer **601** and electrode wiring **301** on substrate **101**, similarly n-type thermoelectric material wafer **601** and electrode wiring **301** on substrate **101** are also connected.

In a cutting and removing process (d), connected thermoelectric material wafer **601** is cut and removed as needed basis such that electrode wirings **301**, to which different types of thermoelectric material chips should be connected, emerge. Through the cutting and removing process (d), substrate **101** is prepared. On the substrate **101**, p-type thermoelectric material chip **603** is connected to predetermined electrode wiring **301**, and electrode wiring **301**, to which n-type thermoelectric material chip **603** should be connected, emerges on the surface of substrate **101**. Similarly, substrate **101** is prepared. On substrate **101**, n-type thermoelectric material chip **603** is connected to predetermined electrode wiring **301n**, and an electrode, to which a p-type thermoelectric material chip should be connected, emerges on the surface of substrate **101**.

In an assembling process (e), for two substrates **101**, surfaces, to each of which thermoelectric material chip **603** is

connected, face each other. Thermoelectric material chips **603** are aligned to predetermined positions where thermoelectric material chips **603** should be connected with electrode wirings **301**. A tip end of thermoelectric material chip **603** of one of substrates **101** is connected to electrode wiring **301**, which corresponds to the chip, on the other substrate **101**. Therefore, the thermoelectric conversion element including the pn junction pair in which the metallic electrode is interposed therebetween is formed (see PTL 2).

However, because a wafer is cut and removed to prepare the thermoelectric material chip whose section is small in a surface which is parallel to the substrate of the thermoelectric material chip, the conventional configuration has a problem in that the chip is broken during the cutting and removing process and during use. Additionally, the thermoelectric material chip is prepared by cutting and removing the wafer, which results in another problem in that the yield of the thermoelectric material is degraded.

In addition to the above thermoelectric conversion element, there is well known a thermoelectric conversion element in which p-type thermoelectric conversion material layers and n-type thermoelectric conversion material layers are alternately stacked with an insulating layer such as the substrate interposed therebetween. A thermoelectric conversion element, in which the p-type thermoelectric conversion material layers and the n-type thermoelectric conversion material layers are electrically connected in series at ends of the layers, is well known as the stacked type thermoelectric conversion element (for example, see PTLs 3 to 9). A thermoelectric conversion element, in which the p-type thermoelectric conversion material layers and the n-type thermoelectric conversion material layers are electrically connected in series at end portions of the layers in a direct manner or by surface contact in which a conductive layer is interposed, is also well known as the stacked type thermoelectric conversion element (for example, see PTLs 10 to 12). A method for forming the Bi₂Te₃ based material on the insulating substrate such as polyimide by sputtering is well known as a method for forming the layer of the thermoelectric conversion material (for example, see PTLs 13 and 14 and NPL 2).

CITATION LIST

Patent Literature

[PTL 1]
Japanese Patent No. 3958857
[PTL 2]
Japanese Patent No. 3592395
[PTL 3]
Japanese Patent Application Laid-Open No. 8-222770
[PTL 4]
Japanese Patent Application Laid-Open No. 11-274581
[PTL 5]
Japanese Patent Application Laid-Open No. 2008-205181
[PTL 6]
Japanese Patent Application Laid-Open No. 50-141287
[PTL 7]
U.S. Pat. No. 3,930,303
[PTL 8]
International Publication No. 05/047560
[PTL 9]
U.S. Patent Application Publication No. 2005/0178424
[PTL 10]
Japanese Patent Application Laid-Open No. 1-93182
[PTL 11]
U.S. Pat. No. 5,055,140

[PTL 12]
U.S. Patent Application Publication No. 2010/0116308
[PTL 13]
Japanese Patent Application Laid-Open No. 2006-86510
[PTL 14]
Japanese Patent No. 3927784

Non Patent Literature

[NPL 1]
IEICE Transactions C Vol. J75-C2 No. 8 pp. 416-424
[NPL 2]
Mitsuyoshi Sakai et al., "Development and research of thermoelectric module on Be—Te based thin film", Proceedings of thermoelectric conversion symposium 2003 (thermoelectric conversion workshop), 2003, p. 24-25

SUMMARY OF INVENTION

Technical Problem

An object of the invention is to provide a thermoelectric conversion element, having many pn junction pairs per unit area and a thermoelectric material chip which is hardly broken, and a producing method thereof.

Solution to Problem

The following thermoelectric conversion element is provided in order to achieve the object.

(1) A thermoelectric conversion element comprising: alternate layers of p-type thermoelectric material layers and n-type thermoelectric material layers; a plurality of substrates disposed between adjacent layers of the p-type thermoelectric material layers and n-type thermoelectric material layers; contact holes respectively provided in the plurality of substrates such that the contact holes appear alternately at opposite ends, in a direction perpendicular to a direction of arrangement of the p-type thermoelectric material layers and the n-type thermoelectric material layers, of the substrates; and a conductive material disposed in the contact holes for electrically connecting the adjacent layers of the p-type thermoelectric material layers and the n-type thermoelectric material layers.

(2) The thermoelectric conversion element described in (1), further comprising high heat-transfer films between adjacent pairs of the plurality of substrates and the p-type thermoelectric material layers.

(3) The thermoelectric conversion element described in (1), further comprising high heat-transfer films between adjacent pairs of the plurality of substrates and the n-type thermoelectric material layers.

(4) The thermoelectric conversion element described in any one of (1) to (3), wherein the plurality of substrates consist of alternate layers of a first substrate and a second substrate, the first substrate having one or more of the p-type thermoelectric material layers formed thereon, the second substrate having one or more of the n-type thermoelectric material layers formed thereon.

(5) The thermoelectric conversion element described in (4), wherein the first substrates include the p-type thermoelectric material layers which are divided into two or more individual segments formed thereon, and the second substrates include the n-type thermoelectric material layers which are divided into two or more individual segments formed thereon.

5

(6) The thermoelectric conversion element described in any one of (1) to (3), wherein both of the p-type thermoelectric material layers and the n-type thermoelectric material layers on the plurality of the substrates are divided into two or more individual segments, respectively.

(7) The thermoelectric conversion element described in any one of (1) to (6), wherein the conductive material includes a projection projecting from the contact hole along the direction of arrangement of the p-type thermoelectric material layers and the n-type thermoelectric material layers, the projection creating a gap between each of adjacent pairs of the p-type thermoelectric material layers and the plurality of substrates or between each of adjacent pairs of the n-type thermoelectric material layers and the plurality of substrates.

The following thermoelectric conversion element producing method is provided in order to achieve the object.

(8) A method for producing a thermoelectric conversion element, comprising:

providing a p-type thermoelectric material layer on one side of a first substrate while making a first contact hole in one end of the first substrate, the first contact hole penetrating through the first substrate;

providing an n-type thermoelectric material layer on one side of a second substrate while making a second contact hole in one end of the second substrate, the second contact hole penetrating through the second substrate; and

stacking the first substrate and the second substrate on top of each other such that the p-type thermoelectric material layer and the n-type thermoelectric material layer appear alternately with the first or second substrate interposed therebetween, and that the first contact hole and the second contact hole appear alternately on opposite ends, in a direction perpendicular to a direction of arrangement of the p-type thermoelectric material layers and the n-type thermoelectric material layers, of the substrates, wherein adjacent pairs of the p-type thermoelectric material layer and the n-type thermoelectric material layer are electrically connected through the contact hole.

(9) The method described in (8), wherein the step of providing the p-type thermoelectric material layer and the n-type thermoelectric material layer respectively on the first substrate and the second substrate is followed by the step of making the first contact hole and the second contact hole respectively in the first substrate and the second substrate, the method further comprises disposing a conductive material in the first contact hole and the second contact hole for electrically connecting the adjacent pairs of the p-type thermoelectric material layer and the n-type thermoelectric material layer.

(10) The method described in (8), wherein the step of making the first contact hole and the second contact hole respectively in the first substrate and the second substrate is followed by the step of providing the p-type thermoelectric material layer and the n-type thermoelectric material layer respectively on the first substrate and the second substrate;

wherein the adjacent pairs of the p-type thermoelectric material layer and the n-type thermoelectric material layer are electrically connected by the p-type thermoelectric material layer and the n-type thermoelectric material layer, the p-type thermoelectric material layer and the n-type thermoelectric material layer extending as far as to backsides of the first substrate and second substrate through wall surfaces of the first contact hole and the second contact hole.

Advantageous Effects of Invention

In the invention, the thermoelectric conversion element comprises the alternate layers of the p-type thermoelectric

6

material layers and the n-type thermoelectric material layers, and the plurality of substrates disposed between adjacent layers of the p-type thermoelectric material layers and n-type thermoelectric material layers. Therefore, the number of pn junction pairs per unit area can be increased, and the breakage of the thermoelectric material chip can be suppressed.

In the invention, the contact holes are alternately disposed at opposite ends of the substrates in the direction perpendicular to the direction of arrangement of the p-type thermoelectric material layers and the n-type thermoelectric material layers, and the conductive material is disposed in the contact holes. The stress applied to each thermoelectric material layer is reduced, because each thermoelectric material layer and the conductive material come easily and securely into contact with each other when the substrates are stacked. Therefore, the substrate and each thermoelectric material layer can be formed thinner. Accordingly, the number of pn junction pairs per unit area can be increased.

In the thermoelectric conversion element of the invention, the plurality of substrates are disposed between adjacent layers of the p-type thermoelectric material layers and n-type thermoelectric material layers, and the contact holes are disposed alternately at opposite ends of the substrates. Therefore, productivity is enhanced in the thermoelectric conversion element of the invention compared with the case in which the p-type thermoelectric material layer and the n-type thermoelectric material layer, which are alternately stacked with the substrate interposed therebetween, are connected by the electrode formed at the edge like the conventional thermoelectric conversion element.

According to the thermoelectric conversion element of the invention, the number of pn junction pairs per unit area is increased because the p-type thermoelectric material layers and the n-type thermoelectric material layers are formed into a layered shape. Therefore, the high output can be obtained. Because the plurality of substrates are disposed between adjacent layers of the p-type thermoelectric material layers and n-type thermoelectric material layers, reliability degradation caused by the breakage of the thermoelectric material can be prevented irrespective of the thermoelectric material.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a view illustrating a schematic configuration of a thermoelectric conversion element according to Embodiment 1 of the invention.

FIG. 2 is a view illustrating a schematic configuration of a thermoelectric conversion element according to Embodiment 2 of the invention.

FIG. 3 is a view illustrating a method for producing the thermoelectric conversion element according to Embodiment 2 of the invention.

FIG. 4 is a view illustrating another method for producing the thermoelectric conversion element according to Embodiment 2 of the invention.

FIG. 5 is a view illustrating a schematic configuration of a thermoelectric conversion element according to Embodiment 3 of the invention.

FIG. 6 is a view illustrating a schematic configuration of a thermoelectric conversion element according to Embodiment 4 of the invention.

FIG. 7 is a view illustrating a method for producing the thermoelectric conversion element according to Embodiment 4 of the invention.

FIG. 8 is a perspective view of a conventional thermoelectric conversion element described in PTL 1.

FIG. 9 is a view illustrating a method for producing a conventional thermoelectric conversion element described in PTL 2.

DESCRIPTION OF EMBODIMENTS

Now, embodiments of the present invention will be described in detail with reference to the accompanying drawings. In the drawings, particularly “p” is affixed to a configuration relating to a p-type thermoelectric material layer, and “n” is affixed to a configuration relating to an n-type thermoelectric material.

Embodiment 1

FIGS. 1A and 1B are a schematic configuration of thermoelectric conversion element 100 according to Embodiment 1 of the invention. FIG. 1A is a perspective view, and FIG. 1B is a sectional view taken on a line A-A of FIG. 1A.

As illustrated in FIG. 1, thermoelectric conversion element 100 of Embodiment 1 includes plural substrates 101 (i.e., p-substrates 101p and n-substrates 101n), and alternate layers of p-type thermoelectric material layer 102p and n-type thermoelectric material layer 102n. The plurality of substrates 101 are disposed between adjacent layers of p-type thermoelectric material layer 102p and n-type thermoelectric material layer 102n. The plurality of substrates 101 have contact holes 103 such that contact holes 103 are disposed alternately at opposite ends, in the direction perpendicular to the direction of arrangement of p-type thermoelectric material layer 102p and n-type thermoelectric material layer 102n, of substrates 101. In FIG. 1, the sign X designates the direction of arrangement of p-type thermoelectric material layer 102p and n-type thermoelectric material layer 102n. In FIG. 1, the sign Y designates the direction perpendicular to the X-direction. In FIG. 1, the sign Z designates a direction orthogonal to both the X-direction and the Y-direction.

For example, substrate 101p, that is adjacent to p-type thermoelectric material layer 102p on one side in the X-direction, includes contact hole 103p in one end portion in the Y-direction. On the other hand, substrate 101n, that is adjacent to p-type thermoelectric material layer 102p on the other side in the X-direction, includes contact hole 103n in the other end portion in the Y-direction. Conductive material 104 is disposed in contact hole 103, and conductive material 104 electrically connects the adjacent layers of p-type thermoelectric material layer 102p and n-type thermoelectric material layer 102n, which are adjacent to each other with substrate 101 interposed therebetween.

Preferably substrate 101 is formed into a film shape. Use of the thin film as substrate 101 can reduce an occupied volume of an insulating substrate in the thermoelectric conversion element, and an occupied volume of a thermoelectric material can be increased. Therefore, the number of pn junction pairs per unit area can be increased, and a higher-voltage output can be obtained.

Preferably a material having a high heat-resistant property is used as a material of substrate 101. The material of substrate 101 may be an inorganic material or a heat-resistant resin such as polyimide. The material having the high heat-resistant property is used as the material of substrate 101, which allows a temperature range to be widened to a higher temperature during production and use of the thermoelectric conversion element. For example, a polyimide film having a thickness of 1 to 100 μm can be used as substrate 101. As to dimensions of substrate 101, for example, a length in the

Y-direction ranges from 1 to 5 mm, and a length in the Z-direction ranges from 10 to 50 mm.

Each of p-type thermoelectric material layer 102p and n-type thermoelectric material layer 102n is a material layer in which an electromotive force is generated when a temperature difference is generated at both ends thereof. A material for the thermoelectric material layer can be selected according to the temperature difference that is generated during use of the thermoelectric conversion element. For example, a bismuth-tellurium based material (Bi—Te based material) can be used as the material when the temperature difference ranges from room temperature to 500 K, a lead-tellurium system (Pb—Te system) can be used as the material when the temperature difference ranges from room temperature to 800 K, and a silicon-germanium system (Si—Ge system) can be used as the material when the temperature difference ranges from room temperature to 1,000 K.

For example, the materials for the p-type and n-type thermoelectric material layers can be obtained by adding a proper dopant to the above material. An example of the dopant, used to obtain the material of the p-type thermoelectric material layer, may include Sb. An example of the dopant, used to obtain the material of the n-type thermoelectric material layer, may include Se. The above material forms a mixed crystal by the addition of the dopant. Accordingly, the dopant is added to the above material in an amount of such that the dopant is expressed in a composition formula of the above material such as “ $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ ” and “ $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ ”.

Preferably the Bi—Te based material that is of the material having excellent performance around room temperature is used as the thermoelectric materials for p-type thermoelectric material layer 102p and n-type thermoelectric material layer 102n.

There is no particular limitation to the thicknesses of thermoelectric material layers 102 and 103. From the viewpoint of increasing the number of pn junction pairs per unit area and obtaining the higher-voltage output, a thin thermoelectric material layer 102 is preferable. From this point of view, an example of the preferable thermoelectric material layer may include a layer having the thickness of 400 to 500 nm. On the other hand, a thick thermoelectric material layer 102 is preferable because a simpler, low-cost process can be selected in forming thermoelectric material layers 102 and 103. Such a thermoelectric material layer having a relatively large thickness can be formed by offset printing, inkjet printing, and plating.

Contact hole 103 is made in substrate 101. At least one contact hole 103 is formed in one end portion or the other end portion in the Y-direction of one p-type thermoelectric material layer 102p or one n-type thermoelectric material layer 102n. One contact hole 103 is preferably made per thermoelectric material layer from the viewpoint of simplification of the process. However, at least two contact holes 103 may be made per thermoelectric material layer, for example, from the viewpoint of stability of a contact state between the substrates stacking one another. There is no particular limitation to a diameter of contact hole 103. However, from the view point of sufficiently introducing conductive material 104 to the inside of contact hole 103, preferably the diameter of contact hole 103 is not lower than 0.8 time the thickness of substrate 101, more preferably the diameter of contact hole 103 is 1 to 10 times the thickness of substrate 101.

In the X-direction, conductive material 104 disposed in contact hole 103 is in contact with both p-type thermoelectric material layer 102p and n-type thermoelectric material layer 102n, which are adjacent to each other with substrate 101 interposed therebetween. Contact hole 103 may be filled with

conductive material **104**, or an inner peripheral wall of contact hole **103** may be covered with conductive material **104**. There is no need to cover a whole surface of the inner peripheral wall of contact hole **103** with conductive material **104**, but it is only necessary that conductive material **104** connects p-type thermoelectric material layer **102p** and n-type thermoelectric material layer **102n**, which are adjacent to each other with substrate **101** interposed therebetween, along an axial direction (X-direction) of contact hole **103**.

For example, conductive material **104** is: a conductive paste such as an Ag paste with which contact hole **103** is filled; a metallic layer such as Cu with which the inner peripheral wall of contact hole **103** is covered; p-type or n-type thermoelectric material layer **102** or **103** which is formed from the surface of substrate **101** such that the inner peripheral wall of contact hole **103** is covered with p-type or n-type thermoelectric material layer **102** or **103**; or a combination of at least two thereof.

The thermoelectric conversion element of Embodiment 1 can be produced as follows. P-type thermoelectric material layer **102p** is formed on substrate **101p** by, for example, sputtering. Similarly n-type thermoelectric material layer **102n** is formed on substrate **101n** by the sputtering.

For example, polyimide having the thickness of 50 μm is used as substrate **101**. On substrate **101**, for example, a layer made of $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.75}$ having the thickness of about 25 to about 30 μm is formed as p-type thermoelectric material layer **102p** by the sputtering, and a layer made of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ having the thickness of about 25 to about 30 μm is formed as n-type thermoelectric material layer **102n** by the sputtering. A target that is prepared by mechanical alloying and pulsed electric current sintering can be used as a target for each thermoelectric material (for example, see NPL 2). In forming p-type and n-type thermoelectric material layers **102p** and **102n**, an RF sputtering apparatus is used, and Ar is used as a sputtering gas. As to sputtering conditions, for example, an output is 40 W, and an Ar gas pressure is in the range from 1×10^{-1} to 1.5×10^{-1} Pa.

After the sputtering, substrate **101** including p-type and n-type thermoelectric material layers **102p** and **102n** may be heated in air, in vacuum, or in an inert gas such as a nitrogen gas. Through the heating, p-type and n-type thermoelectric element layers **102p** and **102n** are stabilized, and electric resistances of p-type and n-type thermoelectric element layers **102p** and **102n** are decreased. Therefore, performance of p-type and n-type thermoelectric element layers **102p** and **102n** can be improved.

Then, contact hole **103p** is made in an end portion of substrate **101p**, and contact hole **103n** is made in an end portion of substrate **101n**. For example, contact hole **103** is made by a usual perforation method such as processing by a laser and a drill, punching, and etching.

Then, conductive material **104** is disposed in contact hole **103**. For example, contact hole **103** is filled with the conductive paste, or contact hole **103** is plated with metal, which allows conductive material **104** to be disposed in contact hole **103**.

Then, substrates **101p** and substrates **101n** are alternately disposed, and therefore p-type thermoelectric material layers **102p** and n-type thermoelectric material layers **102n** are alternately disposed with substrate **101** interposed therebetween. At this point, when contact hole **103p** is disposed in one end portion in the Y-direction of substrate **101p**, contact hole **103n** is disposed in the other end portion in the Y-direction of substrate **101n**.

Along the X-direction, contact holes **103** made in substrates **101** are alternately disposed at one end portion and the

other end portion in the Y-direction by the stacking. As a result, p-type thermoelectric material layer **102p** and n-type thermoelectric material layer **102n**, which are adjacent to each other with substrate **101** interposed therebetween, are electrically connected in series.

Preferably a disposed structure described above is integrated in the thermoelectric conversion element. The disposed structure can be integrated such that an adhesive tape adheres to an end face in the Y-direction over the whole region in the X-direction. Alternatively, the disposed structure can be integrated such that disposed substrates **101** are bounded by a frame body. Alternatively, the disposed structure can be integrated such that p-type thermoelectric material layer **102p**, n-type thermoelectric material layer **102n**, and substrate **101**, which are in contact with one another, are bonded to one another by a bonding agent.

The thermoelectric conversion element is disposed such that the Y-direction of the thermoelectric conversion element is matched with a heat flow direction, which allows the thermoelectric conversion element to be used in power generation by the temperature difference. The thermoelectric conversion element can be used as a temperature control device by passage of a current.

The thermoelectric conversion element has the disposed structure in which p-type thermoelectric material layers **102p** and n-type thermoelectric material layers **102n** are alternately disposed with substrate **101** interposed therebetween. Therefore, the number of pn junction pairs per unit area can be increased, and the breakage of the thermoelectric material chip is hardly generated.

In the thermoelectric conversion element, p-type thermoelectric material layer **102p** and n-type thermoelectric material layers **102n** are electrically connected in series by conductive material **104** disposed in contact hole **103**. The thickness of conductive material **104** is easily controlled because conductive material **104** is disposed in contact hole **103**. Therefore, when substrates **101** are disposed, each thermoelectric material layer **102** and conductive material **104** are easily and securely in contact with each other. Therefore, because a stress applied to each thermoelectric material layer is reduced when substrates **101** are disposed, substrate **101** and each thermoelectric material layer **102** can be formed thinner. From this viewpoint, the number of pn junction pairs per unit area can be increased in the thermoelectric conversion element.

In the thermoelectric conversion element, an electrically-conducting path is formed in the end portion in the Y-direction of substrate **101** by conductive material **104** disposed in contact hole **103**. Different material layers are electrically connected in series by alternately stacking substrates **101** having the different material layers. Therefore, the thermoelectric conversion element can more easily be prepared compared with the conventional thermoelectric conversion element in which the electrodes are formed in the end faces of the stacking object of thermoelectric material layer and the substrate. Accordingly, high productivity is implemented.

The thermoelectric conversion element includes contact hole **103p** that is made at one end portion in the Y-direction of substrate **101p** and contact hole **103n** that is made at the other end portion in the Y-direction of substrate **101n**. Therefore, the thermoelectric conversion element can obtain the high output because the temperature difference between contact hole **103p** and contact hole **103n** is ensured.

In the thermoelectric conversion element, the thermoelectric material layer is formed by the sputtering. The sputtering film is a thin film, and crystal grains of the thermoelectric conversion material constituting the sputtering film become

11

fine. Therefore, in the thermoelectric conversion element, the number of pn junction pairs per unit area can be increased, and the higher output can be obtained.

Embodiment 2

FIGS. 2A and 2B illustrate a schematic configuration of thermoelectric conversion element **200** according to Embodiment 2 of the invention. FIG. 2A is a perspective view, and FIG. 2B is a sectional view taken on a line A-A of FIG. 2A.

As illustrated in FIGS. 2A and 2B, plural substrates **101p** and plural substrates **101n** are alternately disposed in thermoelectric conversion element **200** of Embodiment 2. P-type thermoelectric material layer **102p** is formed in the surface of each of substrates **101p**, and n-type thermoelectric material layer **102n** is formed in the surface of each of substrates **101n**. Plural segments of p-type thermoelectric material layer **102p** are formed in one substrate **101p**. Plural segments of n-type thermoelectric material layer **102n** are formed in one substrate **101n**. As illustrated in FIG. 2A, p-type thermoelectric material layers **102p** and n-type thermoelectric material layers **102n** are respectively arrayed in the Z-direction on each substrate **101**. Each segments of p-type thermoelectric material layer **102p** and each n-type thermoelectric material layer **102n** are formed into a strip, rectangular shape in the Y-direction, respectively. As to dimensions of each rectangular thermoelectric material layer **102**, for example, the length in the Y-direction ranges from 1 to 5 mm, and the length in the Z-direction ranges from 0.05 to 2 mm.

High heat-transfer films **105** having high thermal conductivity (for example, $50 \text{ W}/\{(\text{m}) \times (\text{K})\}$ or more) are formed between substrate **101p** and p-type thermoelectric material layer **102p** and between substrate **101n** and n-type thermoelectric material layer **102n**, respectively. High heat-transfer film **105** may be formed in a whole of one of surfaces of substrate **101**, or high heat-transfer film **105** may be plural strip rectangular films in the Y-direction, which are arrayed in the Z-direction similarly to the thermoelectric material layer as illustrated in FIG. 2A. For example, a thin film or thick film, which is made of Ag (silver), Au (gold), Pd (palladium), Pt (platinum), or W (tungsten), can be used as high heat-transfer film **105**. The thickness of the thin film is, for example, 200 nm.

As illustrated in FIG. 2B, each segments of p-type thermoelectric material layer **102p** and each segments of n-type thermoelectric material layer **102n** are electrically connected by conductive material **104p** disposed in contact hole **103p**. Each segments of p-type thermoelectric material layer **102p** and each segments of n-type thermoelectric material layer **102n** are adjacent to each other with substrate **101**, for example, substrate **101p**, interposed therebetween. Contact hole **103p** of substrate **101p** is formed at one end portions in a lengthwise direction (Y-direction). Contact hole **103n** of substrate **101n** is formed at the other end portion in the lengthwise direction (Y-direction).

Contact hole **103** is filled with conductive material **104**. As illustrated in FIG. 2B, conductive material **104** is projected from an end on one side (side of substrate **101**) in the X-direction of contact hole **103**. Therefore, a gap exists between substrate **101** and p-type thermoelectric material layer **102p** or n-type thermoelectric material layer **102n**, which exists on one side in the X-direction.

An example of a method for producing thermoelectric conversion element **200** of Embodiment 2 will be described below with reference to FIGS. 3A to 3D.

12

A metal mask (not illustrated) is placed over polyimide substrate **101**, and high heat-transfer film **105** is formed into a predetermined shape on substrate **101** by, for example, the sputtering.

While the metal mask is placed, each of segments of p-type thermoelectric material layer **102p** or each of segments of n-type thermoelectric material layer **102n** is formed into the predetermined shape on high heat-transfer film **105** by the sputtering. In Embodiment 2, high heat-transfer film **105** and p-type thermoelectric material layer **102p** or n-type thermoelectric material layer **102n** are formed by the sputtering. Alternatively, high heat-transfer film **105** and p-type thermoelectric material layer **102p** or n-type thermoelectric material layer **102n** may be formed by an evaporation method or a plasma CVD method.

High heat-transfer film **105**, p-type thermoelectric material layer **102p**, and n-type thermoelectric material layer **102n** are formed into the predetermined shape divided the surface shape of substrate **101** into plural segments by placing the metal mask over the substrate, respectively. Alternatively, after high heat-transfer film **105**, p-type thermoelectric material layer **102p**, and n-type thermoelectric material layer **102n** are formed over the substantially whole surface of substrate **101**, high heat-transfer film **105**, p-type thermoelectric material layer **102p**, and n-type thermoelectric material layer **102n** may partially be removed to divide into plural segments by laser irradiation, cutting, etching, and the like.

SUS 304 can be used as a material for the metal mask. However, the material is not limited to SUS 304. In consideration of a heat-resistant property and workability, the material for the metal mask may be selected according to an intended deposit condition or shape.

Then, contact hole **103** is made in substrate **101** on which thermoelectric material layer **102** is formed. A hole is pierced through substrate **101** by the method such as the processing by the laser and the drill, the punching, and the etching, thereby making contact hole **103**. The hole may be made by overlapping plural substrates **101** and piercing through all of the overlapped substances **101**, when the dispositions and shapes of p-type thermoelectric material layers **102p** and n-type thermoelectric material layers **102n** in each substrate **101** are symmetrical in each of the Y-direction and the Z-direction.

Then, conductive material **104** is disposed in contact hole **103**. For example, contact hole **103** is filled with the conductive paste such as the Ag paste, thereby disposing conductive material **104** in contact hole **103**. As illustrated in FIG. 3C, an end of conductive material **104** on the side of the thermoelectric material layer is formed so as to be flush with the surface of contact hole **103**. A projection is projected from contact hole **103** at an end of the conductive material **104** on the side of substrate **101**. For example, a projected length of the projection ranges from 0.01 to 1 μm .

For example, while or after contact hole **103** is filled with the conductive paste, a plate, having a hole whose diameter is substantially identical to that of contact hole **103** and a desired thickness, is overlapped with substrate **101** to surround contact hole **103** by the plate, and the excess paste is removed along the surface of the plate, and the plate is taken off from substrate **101**, which allows the projection to be formed.

Then, substrates **101p** and substrates **101n** are alternately disposed. Segments of p-type thermoelectric material layer **102p** are formed in the surface of each of substrates **101p**, and segments of n-type thermoelectric material layer **102n** are formed in the surface of each of substrates **101n**. At this point, contact hole **103p** of substrate **101p** is disposed at one end

13

portion in the Y-direction. Contact hole **103n** of substrate **101n** is disposed at the other end portion in the Y-direction.

Each of segments of thermoelectric material layer **102p** and each of segments of n-type thermoelectric material layer **102n** are electrically connected in series along the X-direction with conductive material **104** interposed therebetween by stacking substrates **101**. Segments of p-type thermoelectric material layer **102p** on one substrate **101p** and segments of n-type thermoelectric material layer **102n** on one substrate **101n** are arrayed in the Z-direction, respectively. All of the disposed segments of thermoelectric material layer **102p** and **102n** constituting the disposed groups in the X-direction are electrically connected in series by conductive materials **104** disposed in contact holes **103**.

Similarly to the thermoelectric conversion element of Embodiment 1, each thermoelectric material layer and the substrate are integrated by the adhesion of the adhesive tape to the end face in the Y-direction, the binding by the frame body, or the bonding of the projection and the thermoelectric material layer by the bonding agent, thereby forming the thermoelectric conversion element. The thermoelectric conversion element is disposed such that the Y-direction of the thermoelectric conversion element is matched with a heat flow direction, which allows the thermoelectric conversion element to be used in the power generation by the temperature difference. The thermoelectric conversion element can be used as the temperature control device by the passage of the current.

The thermoelectric conversion element of Embodiment 2 has the same effect as that of Embodiment 1 in the same configuration as that of Embodiment 1.

Preferably only p-type thermoelectric material layer **102p** is formed in substrate **101p**, and only n-type thermoelectric material layer **102n** is formed in substrate **101n**. All the thermoelectric material layers are formed on one substrate **101** only by the p-type thermoelectric material layers or the n-type thermoelectric material layers. Therefore, the number of processes can be decreased in manufacturing the thermoelectric material compared with the case in which both the p-type and n-type thermoelectric material layers are formed on one substrate **101**.

In the thermoelectric conversion element, plural segments of p-type thermoelectric material layer **102p** are formed on one substrate **101p**, and plural segments of n-type thermoelectric material layers **102n** are formed on one substrate **101n**. Therefore, the number of pn junction pairs per unit area can further be increased, and the higher output can be obtained.

In the thermoelectric conversion element, conductive material **104** includes the projection projected from contact hole **103**. Therefore, the gap is formed between thermoelectric material layer **102** and substrate **101**. The existence of the gap can reduce the thermal conductivity between a high-temperature end and a low-temperature end of thermoelectric material layer **102** during the use of thermoelectric conversion element **200**, and the higher output can be obtained.

The thermoelectric conversion element also includes high heat-transfer film **105** that is provided between thermoelectric material layer **102** and substrate **101**. During the deposition of thermoelectric material layer **102**, the provided high heat-transfer film **105** promotes a crystal orientation of the thermoelectric material of thermoelectric material layer **102**. During the deposition of thermoelectric material layer **102**, the thermoelectric material is rapidly quenched on high heat-transfer film **105**, whereby a crystal grain of the thermoelectric material becomes finer. Therefore, the thermoelectric performance of the thermoelectric material layer **102** is further improved, and the higher output can be obtained.

14

In Embodiment 2, the Bi—Te based material is used as thermoelectric material layer **102**. There is no particular limitation to the material for thermoelectric material layer **102**, but the material may arbitrarily be changed according to a usage environment or an intended use of thermoelectric conversion element **200**.

In Embodiment 2, contact hole **103** is made after thermoelectric material layer **102** is deposited on substrate **101**. Alternatively, in the invention, contact hole **103** may be made in substrate **101** before thermoelectric material layer **102** is deposited. In this case, the electric conduction of contact hole **103** can simultaneously be established with formation of high heat-transfer film **105** and thermoelectric material layer **102** performed after perforation of contact hole **103**.

A method for establishing the electric connection will be described below by taking an embodiment, in which the thermoelectric material layer is directly formed on substrate **101**, as an example.

As illustrated in FIGS. 4A to 4C, contact hole **103** is made in substrate **101** (FIG. 4A). Then thermoelectric material layer **102** is deposited by the sputtering. The thermoelectric material goes partially round to the back side of substrate **101** while adhering to the inner wall of contact hole **103**. Therefore, the thermoelectric material adheres to an opening edge (on the side of substrate **101** in the X-direction) of contact hole **103** (FIG. 4B). The thermoelectric material adhering to the opening edge forms the projection. That is, the thermoelectric material, that adheres to the inside of contact hole **103** and that forms the projection, constitutes the conductive material.

When substrates **101** including the thermoelectric material layers are disposed, the projection of the thermoelectric material is in contact with each thermoelectric material layer as illustrated in FIG. 4C. Along the X-direction, the projections are alternately disposed in one end portion and the other end portion in the Y-direction. From the viewpoint of simplifying the process, the projection is more effectively made of the thermoelectric material.

In the method illustrated in FIGS. 4A to 4C, the thermoelectric material layer may be deposited after contact hole **103** is made in substrate **101** including the high heat-transfer film **105**. According to the method, the thermoelectric conversion element, which includes high heat-transfer film **105** while the thermoelectric material is used as the conductive material, can be produced.

Conductive material **104** may further be disposed in contact hole **103** in which the thermoelectric material is disposed. In this case, the thermoelectric material also acts as an underlying layer of conductive material **104**. Therefore, effectively conductive material **104** is more strongly disposed in contact hole **103**.

The material for high heat-transfer film **105** is used instead of the thermoelectric material, and high heat-transfer film **105** is formed in substrate **101** in which contact hole **103** is made, which allows the material for high heat-transfer film **105** to be used as the conductive material similarly to the thermoelectric material in the above method.

Embodiment 3

In the thermoelectric conversion element of the invention, the p-type thermoelectric material layers and the n-type thermoelectric material layers are alternately disposed along the X-direction, the disposition of the contact hole may vary in the Y-direction, and the disposition of the thermoelectric material layer may vary in the Z-direction on the same substrate.

15

For example, in thermoelectric conversion element 300 illustrated in FIG. 5, p-type thermoelectric material layers 102p and n-type thermoelectric material layers 102n are alternately arrayed along the X-direction. On one substrate 101', segments of p-type thermoelectric material layers 102p and segments of n-type thermoelectric material layers 102n are alternately disposed along the Z-direction, respectively. For example: a segment of p-type thermoelectric material layer 102p that includes contact hole 103p on one end side in the Y-direction; a segment of n-type thermoelectric material layer 102n that includes contact hole 103n on one end side; a segment of p-type thermoelectric material layer 102p' that includes contact hole 103p on the other end side; and a segment of n-type thermoelectric material layer 102n' that includes contact hole 103n on the other end side; are disposed along the Z-direction on one substrate 101'. Thus, the positions in the Y-direction of contact holes 103 of the thermoelectric material layers vary on one substrate 101'. Along the X-direction, contact holes 103 are alternately disposed in one end portion and the other end portion in the Y-direction.

Thermoelectric conversion element 300 can be produced by the method of FIGS. 3A to 3D except that segments of p-type thermoelectric material layers 102p and segments of n-type thermoelectric material layers 102n are alternately disposed along the Z-direction on substrate 101' and that contact hole 103 is located in one end portion or the other end portion in the Y-direction according to a type of each thermoelectric material layer. Thermoelectric conversion element 300 of Embodiment 3 has the same effect as that of Embodiments 1 and 2 in the same configuration as that of Embodiments 1 and 2.

In the thermoelectric conversion element of the invention, the contact holes may alternately be disposed in one end portion and the other end portion in the Y-direction along the X-direction, and there is no need to form all the contact holes in one end portion in one substrate 101.

In addition to the embodiment of FIG. 5, for example, on the same substrate, all contact holes 103p corresponding to p-type thermoelectric material layers 102p may be made in one end portion in the Y-direction of substrate 101 while all contact holes 103n corresponding to n-type thermoelectric material layers 102n are made in the other end portion in the Y-direction of substrate 101.

Embodiment 4

FIGS. 6A and 6B illustrate a schematic configuration of a thermoelectric conversion element according to Embodiment 4 of the invention. FIG. 6A is a perspective view, and FIG. 6B is a sectional view taken on a line A-A of FIG. 6A.

As illustrated in FIGS. 6A and 6B, plural substrates 101a in each of which p-type thermoelectric material layer 102p and n-type thermoelectric material layer 102a are formed in the surface thereof and plural substrates 101b in each of which the thermoelectric material layer 102 is not formed are alternately disposed in thermoelectric conversion element 400 of Embodiment 4. P-type thermoelectric material layer 102p is formed in one of two surfaces of substrate 101a, and n-type thermoelectric material layer 102n is formed in the other surface of substrate 101a.

In each thermoelectric material layer, similarly to Embodiment 2, the plural strip, rectangular layers in the Y-direction are arrayed along the Z-direction. High heat-transfer films 105 are formed between substrate 101a and p-type thermoelectric material layer 102p and between substrate 101a and n-type thermoelectric material layer 102n, respectively.

16

Contact hole 103a that pierces through p-type thermoelectric material layer 102p, n-type thermoelectric material layer 102n, and substrate 101a is made in one end portion in the Y-direction of substrate 101a. Contact hole 103b that pierces through substrate 101b is made in the other end portion in the Y-direction of substrate 101b.

Conductive material 104a is disposed in contact hole 103a. Conductive material 104a includes the projection only at one end on the side of n-type thermoelectric material layer 102n. The projection is in contact with the surface of substrate 101b.

Conductive material 104b is disposed in contact hole 103b. Conductive material 104b includes the projections that are projected from the surfaces of substrate 101b at both ends in the X-direction. The projection is in contact with p-type thermoelectric material layer 102p at one end in the X-direction, and is in contact with n-type thermoelectric material layer 102n at the other end in the X-direction.

The gaps each having an interval which is the same length as the projected length of the projection are formed between substrate 101b and p-type thermoelectric material layer 102p and between substrate 101b and n-type thermoelectric material layer 102n, respectively. The projection of conductive material 104a in contact hole 103a acts as a spacer. The projection of conductive material 104b in contact hole 103b acts as the spacer and an electric contact of p-type thermoelectric material layer 102p and n-type thermoelectric material layer 102n, between which substrate 101b is sandwiched in the X-direction.

A method for producing thermoelectric conversion element 400 of Embodiment 4 will be described below with reference to FIGS. 7A to 7D.

A metal mask (not illustrated) is placed over polyimide substrate 101a, and segments of high heat-transfer film 105 are formed into a predetermined shape on both surfaces of substrate 101a by the sputtering, respectively (FIG. 7A).

Segments of P-type thermoelectric material 102p are formed on high heat-transfer film 105, which is formed on one of two surfaces of substrate 101a, into the substantially same shape as high heat-transfer film 105 by the sputtering, and segments of n-type thermoelectric material 102n are formed on high heat-transfer film 105, which is formed on the other surface of substrate 101a, into the substantially same shape as high heat-transfer film 105 by the sputtering, respectively (FIG. 7B).

Then, contact hole 103a is made in an end portion of substrate 101a. On the other hand, substrate 101b is prepared, and contact hole 103b is made in an end portion of substrate 101b. Holes are made in substrates 101a and 101b by the method such as the processing by the laser and the drill, the punching, and the etching, thereby making contact holes 103a and 103b. Conductive material 104a that includes the projection at one end in the X-direction is disposed in contact hole 103a. Conductive material 104b that includes the projections at both ends in the X-direction is disposed in contact hole 103b (FIG. 7C).

For example, conductive material 104a is formed by the following method. Contact hole 103a is sufficiently filled with the conductive paste. The end face on the side of p-type thermoelectric material layer 102p is formed so as to be flush with the surface of p-type thermoelectric material layer 102p. The end face on the side of n-type thermoelectric material layer 102n is formed so as to be projected from the surface of n-type thermoelectric material layer 102n by a desired length. Therefore, conductive material 103a that includes the projection at the end on the side of n-type thermoelectric material layer 102n is formed.

17

Similarly, conductive material **104b** is formed by the following method. Contact hole **103b** is sufficiently filled with the conductive paste. Both ends of the conductive paste with which the contact hole **103b** is filled are formed so as to be projected from the surfaces of substrate **101b** by desired lengths. Therefore, conductive material **104b** that includes the projections in both surfaces of substrate **101b** is formed.

Then substrates **101a** in each of which thermoelectric material **102** is formed and substrates **101b** in each of which thermoelectric material **102** is not formed are alternately disposed in the X-direction (FIG. 7D). In this case, substrates **101a** and substrates **101b** are alternately disposed such that contact hole **103a** of substrate **101a** is disposed on one end side in the Y-direction, and such that contact hole **103b** of substrate **101b** is disposed on the other end side in the Y-direction. Therefore, p-type thermoelectric material layers **102p** and n-type thermoelectric material layers **102n** are alternately disposed with substrate **101a** or substrate **101b** interposed therebetween. Each of segments of P-type thermoelectric material layer **102p** and each of segments of n-type thermoelectric material layer **102n** are electrically connected in the X-direction, and are alternately connected at one end portion and the other end portion in the Y-direction. The gaps are formed between p-type thermoelectric conversion element **102p** and substrate **101b** and between n-type thermoelectric material layer **102n** and substrate **101b** by the projections of conductive materials **104a** and **104b**.

The thermoelectric conversion element of Embodiment 4 has the same effect as that of Embodiments 1 to 3 in the same configuration as that of Embodiments 1 to 3. In the thermoelectric conversion element of Embodiment 4: substrate **101a**; p-type thermoelectric material layer **102p**; n-type thermoelectric material layer **102n**; and conductive material **104a** that electrically connects the thermoelectric material layers; are integrally formed. Therefore, compared with Embodiment 2, Embodiment 4 is more effective from the viewpoint of enhancing reliability of the electric connection.

In the thermoelectric conversion element of Embodiment 4, conductive material **104a** includes the projection at one end in the X-direction, and the projection is in contact with substrate **101b**. Therefore, on one side in the X-direction, the gap between substrate **101a** and substrate **101b** is retained by the two projections. Accordingly, from the viewpoint of maintaining the disposed state having the gap, Embodiment 4 is more effective compared with an embodiment in which the gap is retained by the one projection.

This application is based on and claims the benefit of priority from the Japanese Patent Application No. 2011-035648, filed on Feb. 22, 2011, the entire contents of which are incorporated herein by reference.

INDUSTRIAL APPLICABILITY

In the thermoelectric conversion element of the invention and the producing method thereof, the number of thermoelectric material chip pairs per unit area can be increased, and the chip is hardly broken.

REFERENCE SIGNS LIST

100, 200, 300, 400 Thermoelectric conversion element
101, 101', 101p, 101n, 101a, 101b, 803 Substrate
102p, 102p' P-type thermoelectric material layer
102n, 102n' N-type thermoelectric material layer
103a, 103b, 103p, 103n Contact hole
104a, 104b, 104p, 104n Conductive material
105 High heat-transfer film

18

301 Electrode wiring
601 Thermoelectric material wafer
602 Solder bump
603 Thermoelectric material chip
801 Current introduction terminal (positive electrode)
802 Current introduction terminal (negative electrode)
804 P-type thermoelectric material
805 N-type thermoelectric material
806 Junction electrode

H Arrow indicating heat flow direction

The invention claimed is:

1. A thermoelectric conversion element comprising:

first substrates having p-type thermoelectric material layers formed on p-substrates;

second substrates having n-type thermoelectric material layers formed on n-substrates; and

conductive materials connecting adjacent layers of the p-type thermoelectric material layers and the n-type thermoelectric material layers;

wherein the first substrates and the second substrates are alternately disposed such that the p-substrates and the n-substrates are disposed between adjacent layers of the p-type thermoelectric material layers and n-type thermoelectric material layers;

the p-substrates and the n-substrates have contact holes respectively provided in the p-substrates and the n-substrates such that the contact holes appear at ends of the p-substrate and n-substrate, in a direction perpendicular to a direction of arrangement of the p-type thermoelectric material layers and the n-type thermoelectric material layers; and

the conductive materials are disposed in the contact holes and penetrate through the p-type thermoelectric layers or the n-type thermoelectric material layers.

2. The thermoelectric conversion element according to claim 1, further comprising high heat-transfer films between adjacent pairs of the p-substrates and the p-type thermoelectric material layers.

3. The thermoelectric conversion element according to claim 1, further comprising high heat-transfer films between adjacent pairs of the n-substrates and the n-type thermoelectric material layers.

4. The thermoelectric conversion element according to claim 1, wherein

the p-type thermoelectric material layers are divided into two or more individual segments formed on the p-substrates, and

the n-type thermoelectric material layers are divided into two or more individual segments formed on the n-substrates.

5. The thermoelectric conversion element according to claim 1, wherein both of the p-type thermoelectric material layers and the n-type thermoelectric material layers on the p-substrates and the n-substrates are divided into two or more individual segments, respectively.

6. The thermoelectric conversion element according to claim 1, wherein:

each of the conductive materials includes a projection projecting from the contact holes along the direction of arrangement of the p-type thermoelectric material layers and the n-type thermoelectric material layers; and

the projection creates a gap between adjacent pairs of the p-type thermoelectric material layers and the n-substrates or a gap between adjacent pairs of the n-type thermoelectric material layers and the p-substrates.

7. The thermoelectric conversion element according to claim 1, wherein:

19

the p-type thermoelectric material layers and the n-type thermoelectric material layers are extending as far as to backsides of the first substrates and the second substrates through first contact holes and second contact holes respectively, and

adjacent pairs of the p-type thermoelectric material layers and the n-type thermoelectric material layers are electrically connected.

8. The thermoelectric conversion element according to claim 1, wherein the contact holes appear alternately at opposite ends of the p-substrate and n-substrate.

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20